

COMMENTS

Comment on “Noncovalent functionalization of carbon nanotubes by aromatic organic molecules” [Appl. Phys. Lett. 82, 3746 (2003)]

P. Giannozzi^{a)}

NEST-INFM, Scuola Normale Superiore di Pisa, Piazza dei Cavalieri 7, I-56126 Pisa, Italy

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Zhao *et al.*¹ have calculated the interactions of various aromatic molecules with carbon nanotubes, using density-functional theory (DFT). They find evidence of noncovalent functionalization of carbon nanotubes, consisting in a weak chemisorption with a small but sizable charge transfer from the nanotube to the molecule, or vice versa. The charge transfer and associated change of the density of states at the Fermi level would explain the observed sensitivity of transport properties in carbon nanotubes to doping with aromatic molecules. The same mechanism was previously invoked to explain the effects of adsorption of several simple gases (see Refs. 1–12 cited in Ref. 1, in particular Refs. 5, 6, 8, and 9).

The goal of this comment is to show that recent theoretical and experimental work does not support the weak-chemisorption/charge-transfer picture on which Ref. 1 is based.

Let us first focus on the case of O₂ adsorbed on the external wall of a nanotube. Early work (Refs. 5, 6, 8, and 9 of Ref. 1) used the local-density approximation (LDA)—whose drawbacks, in particular the tendency to over-bind, are well known—and ignored spin polarization. When spin polarization is properly taken into account, however, very little charge transfer ($<0.02e$) is found,^{2,3} even when using LDA. Calculations² based on the Perdew–Burke–Ernzerhof flavor of the generalized gradient approximation (GGA) yield very weak binding (~ 0.004 eV) at large C–O distances (~ 3.7 Å). With minor differences, the same pattern holds for other flavors of GGA (Ref. 7 of Ref. 1), unless van der Waals (dispersion) forces are explicitly added.³ Reference 1 finds instead a sizable charge transfer of $0.09e$ at a much smaller C–O equilibrium distance of 2.8 Å with a binding energy of 0.1 eV, using GGA (no mention is made of the treatment of spin polarization).

There is no direct experimental evidence that the effects of O₂ adsorption on transport properties in carbon nanotubes are due to binding of O₂ to the wall of a perfect nanotube. Different mechanisms, such as doping at the contacts, may explain the observed phenomenology.⁴ Recent work shows that O₂ adsorption has no effect at all if impurities are carefully removed from nanotube samples.⁵

The results in Table I of Ref. 1 for both benzene and cyclohexane adsorbed on nanotubes are perfectly consistent

with physisorption, as described by GGA:⁶ large equilibrium molecule–nanotube distance, very small binding energy, no sizable charge transfer. In spite of such evidence, Fig. 4 of Ref. 1 is used to demonstrate hybridization of benzene π states with the nanotube, as opposed to lack of hybridization in cyclohexane. Actually what is shown is that the top valence band includes states having π character that are localized either on the nanotube or on benzene, but this does not imply that there is overlap or hybridization between the two sets of states: simply, their energies are in the same range.

Figure 3 of Ref. 1 shows that for 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) adsorbed on nanotubes, the lowest unoccupied molecular orbital (LUMO) state from DDQ at zone-boundary X point lies just below the top of the valence band of the nanotube. We remark however that even when the DDQ molecule is placed at a large distance from the nanotube (5.3 Å, a distance at which nanotube–molecule interactions are very small), the gap between the LUMO of DDQ and the top of the valence band of the nanotube is ~ 0.1 eV (see Fig. 1). The lineup between the top of the valence band of the nanotube and the LUMO of DDQ is thus mostly determined by the two systems separately and only

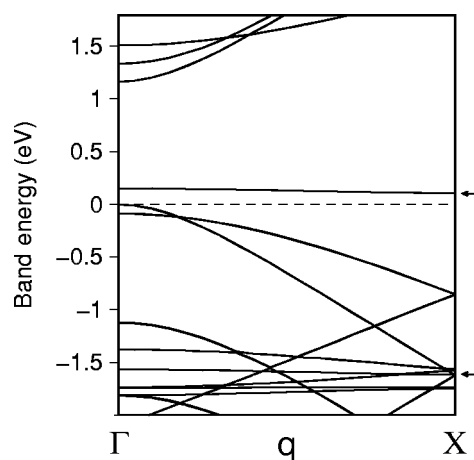


FIG. 1. Band structure along the nanotube axis for a DDQ molecule at 5.3 Å from a (10,0) nanotube. The dashed line is the Fermi energy. The supercell contains 80 nanotube atoms and a DDQ molecule, both in their equilibrium structure. The arrows indicate the positions of bands derived by the highest occupied and lowest unoccupied molecular state of DDQ, respectively.

^{a)}Electronic mail: giannozz@nest.sns.it

marginally modified by their interactions. Whether such lineup can be reliably calculated with current approximations to DFT is not obvious. If we assume that the occupied states of the two systems are correctly lined up, the well-known underestimate of the gap between the highest occupied molecular orbital (HOMO) and the LUMO will lead to an incorrect lineup of unoccupied with occupied states. For DDQ, the calculated HOMO–LUMO gap with GGA is 1.63 eV.

In conclusion, the results of DFT calculations in weakly bound systems like molecules adsorbed on nanotubes should be handled more carefully.

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